Synthesis and Reactions of Tungsten(II) Norbornadiene (nbd) Complexes. The Crystal and Molecular Structure of $[WBr(SC_6F_5)(CO)_2(nbd)]^{\dagger}$

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The reaction of $[WBr_2(CO)_2(nbd)]$ 1 (nbd = norbornadiene) with $TI(C_5H_5)$ gave a monocarbonyl derivative $[WBr(CO)(nbd)(\eta^5-C_5H_5)]$ 2. With $TI(O_2CMe)$ and TI[O(S)CMe], complex 1 gave monosubstituted derivatives $[WBr(O_2CMe)(CO)_2(nbd)]$ 3a and $[WBr{O(S)CMe}(CO)_2(nbd)]$ 3b which appear to be seven-co-ordinate according to IR data. In contrast 1 and $TI(SC_6F_5)$ (1:1 molar ratio) gave the six-co-ordinate complex $[WBr(SC_6F_5)(CO)_2(nbd)]$ 4. An X-ray diffraction study of 4 established that it has a distorted-octahedral structure with *trans* W-CO bonds approximately perpendicular to a plane containing the W, Br and S atoms and the midpoints of the nbd C=C bonds. Simple electronic arguments provide a rationalisation of many of the structural features of 4. Reaction of 1 with 2 molar equivalents of $TI(SC_6F_5)$ gave the bis(thiolate) derivative $[W(SC_6F_5)_2(CO)_2(nbd)]$ 5 again with a *trans* arrangement of CO ligands. The reactions of 5 with L = PEt_3, PMe_2Ph or P(OMe)_3 gave the six-co-ordinate complexes $[W(SC_6F_5)_2(CO)_2L_2]$ 6 which exist in two isomeric forms, red or green. Dynamic NMR studies have been used to characterise the isomeric behaviour and fluxional processes in the complexes.

An interesting feature of divalent molybdenum and tungsten chemistry is the ability of the metal to form either seven-coordinate 18-electron complexes which may be mono- or dinuclear or alternatively co-ordinatively unsaturated six-coordinate derivatives with a formal 16-electron configuration.¹ Although steric factors might be expected to play an important role in determining the relative stability of six- and seven-coordinate derivatives, electronic factors may also be important. For example, formally electron-deficient six-co-ordinate complexes could, in principle, be stabilised by π donation from certain anionic ligands, e.g. halides or oxygen-donor ligands. Previously we reported evidence for sulfur \rightarrow metal π donation in complexes $[M(SC_6F_5)(CO)(CF_3C=CCF_3)(\eta^5-C_5H_5)]^2$ and decided to attempt synthesis of SC_6F_5 complexes of W^{II} by replacement of bromide ligands in the six-co-ordinate complex $[WBr_2(CO)_2(nbd)]$ (nbd = norbornadiene) 1 we reported previously.³ We now report the results of these studies in addition to details of other bromide-substitution reactions. During the course of this work syntheses of molybdenum and tungsten thiolate complexes were reported^{4,5} which provide an interesting comparison with our work.

Results and Discussion

The reaction of complex 1 with $Tl(C_5H_5)$ was carried out in an attempt to isolate a σ - or η^3 -C₅H₅ derivative. However, loss of one molecule of carbon monoxide occurs readily in diethyl ether since the red crystalline product 2 has the stoichiometry [WBr(CO)(nbd)(C₅H₅)] according to mass spectroscopy (m/z = 449, M^+). However, attempts to obtain completely satisfactory data for carbon were unsuccessful (calc. 34.8, found 33.5%) despite the fact that hydrogen analysis was acceptable and the complex was recrystallised several times. The ¹H NMR spectrum showed no trace of impurities and is also



consistent with the above stoichiometry showing a η^5 -C₅H₅ singlet and five norbornadiene resonances, integrated ratio 2:2:1:1:2. The IR spectrum as expected shows one v(CO)mode at 1928 cm⁻¹. Interestingly, attempts to isolate complexes of this type from the reaction of $[MCl(CO)_3(\eta^5-C_5H_5)]$ (M = Mo or W) with norbornadiene were unsuccessful, although butadiene (C₄H₆), $[Mo(CO)_2(C_4H_6)(\eta^5-C_5H_5)]^+$ $[MCl(CO)(C_4H_6)(\eta^5-C_5H_5)]$ (M = Mo or W) and $[MoMe-(CO)(C_4H_6)(\eta^5-C_5Me_5)]^7$ and duroquinone (2,3,5,6-tetramethylcyclohexa-2,5-diene-1,4-dione) complexes [MoCl(CO)- $(C_6Me_4O_2)(\eta^5-C_5H_5)]^8$ are known. The structure of 2 is presumably related to the latter with η^4 co-ordination of the norbornadiene ligand resulting in an 18-electron configuration at the metal. Significantly we note that the ¹H NMR data are incompatible with η^2 co-ordination since the alkene CH proton signals appear in the region δ 3.6–4.7 consistent with approach to sp³ hybridisation as expected for co-ordinated alkene carbons.

The reaction of $[WBr_2(CO)_2(nbd)]$ 1 with 1 molar equivalent of the thallium(1) derivatives $TI(O_2CMe)$ and TI[O(S)-CMe] affords brown or yellow complexes which analyse as monosubstituted derivatives $[WBr(O_2CMe)(CO)_2(nbd)]$ 3a and $[WBr{O(S)CMe}(CO)_2(nbd)]$ 3b. Interestingly, monosubstituted complexes were obtained even when an excess of thallium salt was used. In contrast $[MoBr_2(CO)_2(PPh_3)_2]$ has been found to react with Na[O(S)CR] (R = Me or Ph) to give successively $[MoBr{O(S)CR}(CO)_2(PPh_3)_2]$ and

[†] Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1993, Issue 1, pp. xxiii-xxviii.

 $[Mo{O(S)CR}_2(CO)_2(PPh_3)_2]$.⁹ The spectroscopic properties of 3a and 3b are unexpectedly simple with one very weak and one very strong band in the v(CO) region in the IR spectra somewhat similar to the behaviour of precursor 1.3 The CO ligands in 3 presumably have an approximately *trans* configuration with a OC-W-CO angle slightly less than 180° (cf. 1). The ¹H NMR spectra are also very simple, each giving one methyl resonance in addition to three norbornadiene peaks at room temperature, integrated ratio 2:1:1. The bridgehead CH₂ appears as a pseudo-quartet, *i.e.* two doublets with secondorder distortion. At lower temperatures the peak due to the four equivalent hydrogens shows distinct asymmetry but does not split into clearly resolved separate peaks, even at -80 °C. This would appear to indicate a high-symmetry structure possibly similar to that of complex 1. However, other spectral data suggest otherwise. In principle, six- or seven-co-ordinate structures are possible for these complexes depending on whether the O_2CMe and O(S)CMe ligands are mono- or bi-dentate. Aforementioned molybdenum derivatives [MoBr{O(X)CMe}- $(CO)_2(PPh_3)_2$ (X = O or S) have been assigned seven-coordinate structures on the basis of infrared spectroscopic studies.⁹ The difference (Δ) between $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ is considered to be useful in distinguishing between mono- and bi-dentate carboxylate ligands.¹⁰ If Δ is similar to or smaller than that for $Na(CO_2R)$ then bidentate behaviour can be assumed. In the case of **3a** v(CO₂) modes were observed at 1490m and 1538w, *i.e.* $\Delta = 48 \text{ cm}^{-1}$, thus indicating a chelate structure and therefore seven-co-ordination. We assume that 3b has a similar structure in view of the comparable spectroscopic properties. This is consistent with the presence of a v(CO) mode at 1470 cm⁻¹ which compares with 1480 cm⁻¹ for the seven-coordinate complex $[MoBr{O(S)CPh}(CO)_2(PPh_3)_2]$.

Different isomeric forms are possible for seven-co-ordinate structures but the limited data available do not allow us to comment further. Unfortunately, attempts to obtain suitable crystals for X-ray diffraction studies were unsuccessful. However, we note that seven-co-ordinate structures are frequently fluxional, in many cases with very low energy barriers to rearrangement.¹ This explains the ¹H NMR data where exchange processes may be responsible for the simple appearance of the spectra. Alternatively this may arise from the accidental degeneracy of two or more resonances and studies currently in progress on related derivatives will hopefully resolve this matter.

The reaction of [WBr₂(CO)₂(nbd)] 1 with 1 molar equivalent of $Tl(SC_6F_5)$ in dichloromethane affords a brown crystalline complex which analyses as the monosubstituted derivative $[WBr(SC_6F_5)(CO)_2(nbd)]$ 4. The IR spectrum of 4 shows two v(CO) modes, a very weak band near 2050 cm⁻¹ and a strong mode near 1975 cm⁻¹ which compares closely with the spectrum of the dibromo precursor 1. X-Ray diffraction studies of 1 have established a structure which is basically octahedral with trans carbonyl and cis bromine ligands.¹¹ The octahedron is distorted with a OC-W-CO angle of 172.9(4)°. Consequently the strong asymmetric stretch of the trans CO ligands is accompanied by a weak, high-frequency symmetric stretch activated by the structural distortion. A similar structure is therefore possible for 4 in which the octahedron is distorted as a result of the d^4 configuration of the metal.¹² The trans arrangement of the CO groups is in contrast with the trans, cis geometry of [Mo(SBu')- $(CO)_2(bipy)]^5$ (bipy = 2,2'-bipyridine) and $[Mo(OBu^t)_2-(CO)_2(py)_2]^{13}$ (py = pyridine) where the *cis* carbonyls give rise to two strong bands at significantly lower frequencies. trans-Thiolate ligands have also been found in $[Mo(SBu^{t})_{2}(dppe)_{2}]^{14}$ whereas a *cis* arrangement of anionic ligands has been estab-lished in $[Mo(SBu')_2(CNBu')_4]^{15}$ and $[MoH(SR)(dppe)_2]$ $(R = C_6H_2Pr'_{4}^{-2}-2,4,6; dppe = Ph_2PCH_2CH_2PPh_2)^{16}$ by X-ray diffraction studies.

Although a distorted-octahedral structure seems reasonable for complex 4, the fact that complexes 3 appear to be seven-coordinate raised the possibility that a seven-co-ordinate dimeric

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structure with bridging thiolates was also possible. Consequently X-ray diffraction studies of the complex were carried out. These established a monomeric, six-co-ordinate structure for complex 4 (see Fig. 1 and Table 1). Moreover, there is virtually no change in the highly distorted octahedral coordination of the metal atom in [WBr₂(CO)₂(nbd)] 1 when a bromine atom is replaced by a pentafluorobenzenethiolato ligand. Thus, in 4 the carbonyl ligands are trans [C(7)-W-C(8)]172.7(8)°] and C(nbd1) and C(nbd2), the midpoints of the nbd double bonds C(11)-C(12) and C(14)-C(15), together with the atoms W, Br and S are coplanar to within ± 0.04 Å. Within this plane the deviations of the angles subtended at tungsten from ideal values of 90 or 180° [note especially Br-W-S 108.2(2), C(nbd1)-W-C(nbd2) 64, Br-W-C(nbd1) 155 and S-W-C-(nbd2) 160°] are both substantial and nearly identical to corresponding angles in 1.11

The W–Br bond length in complex 4 [2.521(3) Å], though longer than the corresponding distances in 1 [2.489(1) and 2.493(1) Å],¹¹ is still relatively short compared with values of 2.559(4)–2.571(4) Å found in [WBr₂(CO)₂(PPh₃)₂] where the W atoms adopts a non-octahedral co-ordination,^{11,17} of 2.640(1) Å in [WBr(S₂CNMe₂)(CO)(nbd)(PMe₂Ph)] where the W atom is seven-co-ordinate,¹⁸ and with 2.619 Å, an average W–Br distance derived from the Cambridge Structural



Table 1 Selected bond lengths (Å), angles and torsion angles (°) in $[WBr(SC_6F_5)(CO)_2(nbd)]$ 4

W–Br	2.521(3)	W-S	2.322(5)
W-C(7)	2.040(18)	W-C(8)	1.975(19)
W-C(11)	2.233(21)	W-C(12)	2.279(19)
W-C(14)	2.397(18)	W-C(15)	2.380(17)
W-C(nbd1)	2.148	W-C(nbd2)	2.282
S-C(1)	1.774(17)	O(1)-C(7)	1.138(21)
O(2)-C(8)	1.167(23)	C(9) - C(10)	1.574(29)
C(9) - C(13)	1.510(32)	C(10)-C(11)	1.551(26)
C(10)-C(15)	1.494(28)	C(11)-C(12)	1.382(27)
C(12)-C(13)	1.520(26)	C(13)-C(14)	1.489(28)
C(14)-C(15)	1.408(26)		
Br-W-S	108.2(2)	Br-W-C(7)	85.1(6)
Br-W-C(8)	89.6(6)	BrW-C(nbd1)	155.2
Br-W-C(nbd2)	91.5	S-W-C(7)	91.8(5)
S-W-C(8)	85.2(5)	S-W-C(nbd1)	96.6
S-W-C(nbd2)	160.1	C(7)-W-C(8)	172.7(8)
C(7)-W-C(nbd1)	94.3	C(7)-W-C(nbd2)	92.5
C(8)-W-C(nbd1)	92.7	C(8)-W-C(nbd2)	92.6
C(nbd1)-W-C(nbd2)	63.7	W-S-C(1)	110.6(6)
SC(1)C(2)	123.0(12)	S-C(1)-C(6)	121.2(15)
C(2)-C(1)-C(6)	115.8(16)	WC(7)-O(1)	176.5(16)
W-C(8)-O(2)	174.8(16)	C(10)-C(9)-C(13)	92.5(16)
C(9)-C(10)-C(11)	101.3(15)	C(9)-C(10)-C(15)	100.3(16)
C(11)-C(10)-C(15)	100.9(16)	C(10)-C(11)-C(12)	103.8(15)
C(11)-C(12)-C(13)	108.1(16)	C(9)-C(13)-C(12)	101.0(17)
C(9)-C(13)-C(14)	102.6(17)	C(12)-C(13)-C(14)	101.8(15)
C(13)-C(14)-C(15)	105.3(17)	C(10)-C(15)-C(14)	106.5(15)
Torsion angles			
Br-W-S-C(1)	-87.4(7)	W-S-C(1)-C(2)	84.7(15)
C(7)-W-S-C(1)	-2.0(8)	W-S-C(1)-C(6)	94.9(15)
C(8)-W-S-C(1)	-175.4(8)		
C(nbd1) and C(nbd2) are the m	nidpoints of the C(11)	-C(12) and
C(14)-C(15) bonds.			



Fig. 1 A view of a molecule of [WBr(SC₆F₅)(CO)₂(nbd)] 4 showing 20% vibrational ellipsoids except for hydrogen atoms which are represented by spheres of arbitrary size

Database.¹⁹ A survey of W-Br distances in 37 structures containing Br bonded to six-co-ordinate W confirms that the great majority are longer than that in 4.20 In contrast the W-CO distances in 4 [1.98(2) and 2.04(2) Å], like those in 1 [2.03(1) and 2.05(1) Å], seem relatively long: a mean value of 1.936 Å has been derived for such distances 19 and values of 1.92(3)-1.974(7) Å have been found in [WBr₂(CO)₂-(PPh₃)₂],^{11,17} [WBr(S₂CNMe₂)(CO)(nbd)(PMe₂Ph)]¹⁸ and $[W(SC_6H_2Pr_3-2,4,6)_2(CO)_2(PMe_2Ph)_2]^4$ In the last compound the tungsten co-ordination is trigonal prismatic and this may partly explain why the W-S(thiolate) bond lengths [2.460(2) and 2.395(2) Å] are so much longer than the corresponding distance of 2.322(5) Å in 4. However, we consider that strong $\tilde{S} \rightarrow W \pi$ donation is the major reason for the shortness of the W-S bond in 4. We have previously rationalised variations in W^{IV}-S(thiolate) bond lengths in a similar way.²¹

The most notable structural difference between complexes 1 and 4 lies in the asymmetry shown by the W-C(nbd) distances in the latter. The W-C(11) and W-C(12) bond lengths [2.23(2) and 2.28(2) Å] are comparable with values in other $W^{II}(nbd)$ complexes {e.g. 2.26(1)-2.30(1) Å in 1 and 2.266(5)-2.324(5) Å in $[WBr(S_2CNMe_2)(CO)(nbd)(PMe_2Ph)]^{11,18}$ whereas the W-C(14) and W-C(15) bond lengths [2.40(2) and 2.38(2) Å] are much longer, implying that the thiolate ligand exerts a greater trans influence than does bromide.

Most of the significant structural features of complex 4 can be accounted for by an extension of the arguments advanced by Cotton and Meadows¹¹ to explain the bonding in 1. In this approach the distortions from octahedral co-ordination are ignored in considering the d-orbital splitting of the tungsten(11) ion which is assigned a $d_{xz}^2 d_{yz}^2 d_{xy}^0$ configuration [x, y and z axes in 4 being taken approximately parallel to the W-Br, W-S and C(7) vectors]. Thereby all four metal d electrons are



Fig. 2 Orbital overlap in [WBr(SC₆F₅)(CO)₂(nbd)] 4 showing π donation from sulfur to tungsten

available for donation into π -acceptor carbonyl and nbd orbitals. The empty d_{xy} orbital is thus freed for π donation from S and Br. The structure of 4 is best understood if $S \rightarrow W \pi$ donation predominates (see Fig. 2). The C(7)-W-S-C(1) and W-S-C(1)-C(2) torsion angles of -2.0(8) and $-85(2)^{\circ}$ indicate, on the supposition of sulfur sp² hybridisation, that the filled sulfur p-orbital is aligned in the xy plane. It is thus able to make a maximum overlap with the $\hat{W} d_{xy}$ acceptor orbital whereas it is virtually normal to, and hence unable to interact with, the $C_6F_5\pi$ system. The orientation of the thiolate ligand with respect to the metal, the shortness of the W-S bond and the slightly greater length of the W-Br bond in 4 compared with 1 are all consistent with this bonding scheme. Furthermore, the high trans influence of the thiolate ligand in 4 can be explained by a simple electrostatic argument: the W-C(nbd1) and W-C(nbd2) σ -donor bonds are respectively perpendicular and parallel to the direction of $S \rightarrow W$ charge transfer which should therefore exert a greater weakening effect on W-C(nbd2). The variable-temperature ¹H and ¹⁹F NMR spectra of



Fig. 3 Space-filling and ball-and-stick diagrams of $[WBr(SC_6F_5)(CO)_2(nbd)]$ 4 showing interaction of a C_6F_5 o-fluorine with the CO ligand (circled)

complex 4 can be interpreted in terms of the structure found in the solid state. Below $-20 \,^{\circ}\text{C}$ (CDCl₃) the ¹H spectrum shows six equal intensity resonances at δ 3.5-4.7 and a bridgehead CH_2 peak at δ 0.98. In theory the latter should be split due to inequivalence of the two protons but we assume their distance from the Br and SC_6F_5 ligands results in a single peak. As the temperature is raised the bridgehead CH₂ peak shows little change but the other six broaden (ca. 10 °C) and collapse to give three broad resonances integrated 1:1:1 at ca. 35 °C. In deuteriated toluene a total of four well resolved peaks are observed at +65 °C. These data are consistent with structure 4 which is rigid at low temperatures and where the C_6F_5S ligand adopts a particular orientation with respect to the rest of the molecule, presumably that observed in the solid state. We have observed this previously in pseudo-six-co-ordinate perfluoro-thiolate derivatives of Mo^{II} and W^{II}, $[M(SR)(CO)(CF_3C \equiv CCF_3)(\eta^5-C_5H_5)]$ (M = Mo or W, R = CF₃ or C₆F₅) where two isomers are observed at low temperature in the ¹⁹F NMR spectra due to restricted rotation about the M-SR bond.² We also note that the SC₆H₂Prⁱ₃-2,4,6 ligand in the related complex $[MoH(SC_6H_2Pr^i_3-2,4,6)(dppe)_2]^{16}$ adopts a comparable orientation to that of the SC_6F_5 group in 4 by lying parallel to the MoPSP plane. At higher temperatures rotation about the $W-SC_6F_5$ bond in 4 will result in equivalence of three sets of hydrogens leading to three non-bridgehead peaks in the ¹H NMR spectra, as is observed. The ¹⁹F NMR spectrum of complex **4** is also temperature

dependent, the most definitive information being obtained from the o-fluorine region near δ -130. At room temperature (CD_2Cl_2) a sharp multiplet is observed but below -40 °C this broadens and splits into two broad peaks at -90 °C. The mfluorine resonance is also broad at this temperature whereas the para resonance remains sharp throughout this temperature range. This is also consistent with the existence of one C_6F_5 environment in addition to which a preferred C_6F_5 orientation also appears to be adopted at low temperatures as a consequence of a barrier to rotation about the C₆F₅-S bond. We have observed this previously in $[M(SC_6F_5)O(CF_3C \equiv CCF_3)(\eta^5 \cdot C_5H_5)]$ (M = Mo or W) where steric interactions were held to be responsible.² As with the latter case, molecular graphics studies ²² of 4 revealed steric interactions between the C_6F_5 o-fluorines and the adjacent CO ligand as the former is allowed to rotate about the $S-C_6F_5$ bond (see Fig. 3). Not surprisingly these are at their greatest when the C_6F_5 group is rotated by ca. 90° relative to the position found in the solid state. The preferred orientation is presumably that observed in the solid state which would account for the separate environments observed for the five fluorines of the C₆F₅ ring at low temperatures.

The bis(thiolato) complex $[W(SC_6F_5)_2(CO)_2(nbd)]$ 5, obtained from 1 with 2 molar equivalents of $TI(SC_6F_5)$, forms dark red crystals which are soluble in polar organic solvents such as acetone and dichloromethane. The IR spectrum is



almost identical to those of 1 and 4 showing a weak v(CO) mode at 2040 cm⁻¹ accompanied by a strong band at 1969 cm⁻¹, again indicating a *trans* disposition of CO ligands with a non-linear OC-W-CO arrangement. This dictates a *cis* arrangement of the thiolate ligands which interestingly contrasts with the *trans* structure revealed by X-ray diffraction studies of the related complexes [Mo(SBu')₂(dppe)]¹⁴ and [Mo(SC₆H₃Ph₂-2,6)₂-(CO)₂(bipy)].²³

The ¹H and ¹⁹F NMR spectra of complex 5 are temperature dependent, again indicating restricted rotation about the C_6F_5 -S and C_6F_5S -W bonds. However, the situation is also complicated by isomerism as will now be described. If we assume the existence of sulfur-metal π donation as described earlier for 4 (Fig. 2) it is clear that two isomers are possible, the syn and anti forms. The ¹H and ¹⁹F NMR spectra provide evidence for both forms at low temperature but free rotation about the W-SC₆ F_5 bonds results in isomer exchange at higher temperatures. At 20 °C (CD₂Cl₂) the ¹H NMR spectrum exhibits the three norbornadiene NMR signals, integrated 4:2:2, expected for such a structure. At lower temperatures the two non-bridgehead signals broaden and split into five separate peaks, one of which is composed of overlapping multiplets (Fig. 4). Detailed analysis of these peaks, in particular their integrated intensities, indicates that two isomeric forms are present, ratio 3:4; the syn gives rise to four non-bridgehead resonances ratio 2:2:1:1 and the *anti* isomer to three of equal intensity. The ¹⁹F NMR spectrum (CD_2Cl_2) accordingly shows one C_6F_5 environment at 20 °C but two, ratio 3:4 (one anti and one syn), at -70 °C. Subsequent broadening and splitting of the ofluorine peaks at lower temperatures reveals evidence for restricted rotation about the C_6F_5 -S bonds in both isomers. In contrast distinct peaks due to the syn and anti forms of the related complex cis-[Mo(SBu^t)₂(CNBu^t)₄] could not detected in the ¹H and ¹³C NMR spectra as low as -100 °C¹⁴ suggesting a much lower barrier to exchange compared with 5.

Previously we have observed that $[WBr_2(CO)_2(diene)]$ react with an excess of ligand L to give $[WBr_2(CO)L_2(diene)]$ [diene = nbd, L = PMe₂Ph or P(OMe)₃] whereas with diene = cycloocta-1,5-diene or cyclooctatetraene substitution occurs to give seven-co-ordinate complexes $[WBr_2(CO)_2L_3]$ [L = CNBu^t, P(OMe)₃ or PMe₂Ph].³ Accordingly reactions of $[W(SC_6F_5)_2(CO)_2(nbd)]$ with PEt₃, PMe₂Ph or P(OMe)₃ were carried out. Complex 5 reacts smoothly with an excess of phosphine in diethyl ether or dichloromethane at room temperature to give green (L = PEt₃ or PMe₂Ph) or red [L = P(OMe)₃] solutions from which the dicarbonyl complexes $[W(SC_6F_5)_2(CO)_2L_2]$ (L = PEt₃ 6a, PMe₂Ph 6b or P(OMe)₃ 6c] were isolated. The green and red complexes 6a and 6c appear to be relatively stable in solution, whereas the green form of the PMe₂Ph complex 6b appears to rearrange in solution to give a mixture of red and green forms after *ca*. 30 min according to NMR studies.

These results are similar to those reported for related thiolate complexes $[M(SC_6H_2Pr_{i_3}^3-2,4,6)_2(CO)_2(PMe_2Ph)_2]$ (M = Mo or W, R = Me or Prⁱ) which also exist in red and/or green isomeric forms.⁴ X-Ray diffraction studies of the red complexes $[M(SC_6H_2Pr_{i_3}^3-2,4,6)_2(CO)_2(PMe_2Ph)_2]$ (M = Mo or W) revealed an unusual distorted trigonal-prismatic structure 7a with one $SC_6H_2Pr_{i_3}^3-2,4,6$, one PMe₂Ph and one CO ligand occupying each triangular face. However, NMR data indicate that the structure is closer to octahedral in solution, possibly with the *cis*, *trans*, *cis* structure 7b. The red-brown bipyridyl complex [Mo(SCMe_3)_2(CO)_2(bipy)] has also been assigned a *trans*, *cis*, *cis* octahedral structure on the basis of spectroscopic

T/⁰C

20

-20

-40

-70

3.4

 δ Fig. 4 Variable-temperature ¹H NMR spectra of [W(SC₆F₅)₂(CO)₂-(nbd)] 5 in CD₂Cl₂ (s = syn, a = anti)

3.8

4.2

4.6



3345

data.⁵ Related six-co-ordinate thiolate complexes $[Ru(SR)_2-(CO)_2(PR'_3)_2]^{24}$ and $[Os(SR)_2(CO)_2(PR'_3)_2]^{25}$ are known which have been assigned octahedral geometries.

It seems reasonable to assign a similar solid-state structure 7a to 6c and the red form of 6b in view of the similar colour and stoichiometry to the red complexes [M(SC₆H₂Prⁱ₃-2,4,6)₂(CO)₂(PMe₂Ph)₂]. However, in solution the spectroscopic data are more consistent with an octahedral geometry and a cis OC-W-CO arrangement. For example, the solution IR spectrum of $[W(SC_6F_5)_2(CO)_2{P(OMe)_3}_2]$ 6c shows a medium and a strong v(CO) band at 1978 and 1905 cm⁻¹. This compares with 1940 and 1867 cm⁻¹ for **6b** and 1921 and 1830 cm^{- $\bar{1}$} for [W(SC₆H₂Prⁱ₃-2,4,6)₂(CO)₂(PMe₂Ph)₂]. These differences presumably reflect differences in the donor properties of the thiolate ligands and the phosphorus-donor ligands. Exceptionally low v(CO) values (1908, 1768 cm⁻¹) found with $[Mo(OBu')_2(CO)_2(py)_2]$ have been interpreted in terms of significant π donation by the alkoxide ligands to the metal.13

Based on a distorted-octahedral geometry, three forms with *cis* carbonyls are possible, **6(i)**, **6(ii)** and **6(iii)**. Two of these have been identified in the solid state previously, **6(ii)** in the aforementioned *trans,cis,cis*-[Mo(OBu^t)₂(CO)₂(py)₂]¹³ and **6(iii)** in *cis,cis,trans*-[MoBr₂(CO)₂(PPh₃)₂].²⁶ Moreover isomeric forms of all three (*syn* and *anti*) are also possible as a consequence of preferred C₆F₅S orientations. However, at room temperature only one set of P(OMe)₃, C₆F₅ and CO signals are observed in ¹H, ¹⁹F, ³¹P and ¹³C NMR spectra of **6c** thus eliminating the less-symmetric isomer **6(i)**.

The ${}^{13}C-{}^{1}H$ NMR spectrum of complex 6c shows one $P(OMe)_3$ methyl peak and a triplet for the carbonyl-carbon resonance J_{P-C} 73.5 Hz, consistent with either 6(ii) or 6(iii) in solution. However, the ¹H NMR spectrum exhibits the distinctive 'filled in doublet' observed for cis-P(OMe)₃ methyls when intermediate values of J_{P-P} are present indicating that **6(ii)** is the preferred isomeric form.²⁷ The ¹⁹F NMR spectrum also shows one set of C_6F_5 resonances at room temperature but these broaden at lower temperatures and separate into two sets of peaks, integrated 2:1, at -60 °C in CD₂Cl₂. It appears that two isomers exist at this temperature, the minor one with equivalent C_6F_5 groups, 6(ii) syn and the major species with two C_6F_5 environments, 6(ii) anti. This is supported by the ³¹P-{¹H} NMR spectrum where the singlet observed at 20 °C splits into one sharp and one broad peak at -60 °C. This structural proposal differs from that suggested for red $[W(SC_6H_2Pr^i_3-2,4,6)_2(CO)_2(PMe_2Ph)_2]$ where structure 7b is proposed despite the fact that the IR spectrum indicates cis carbonvls.4

Possible structures of the green complexes [M(SC₆H₂Me₃- $2,4,6)_2(CO)_2(PMe_2Ph)_2]$ (M = Mo or W) have been discussed in detail by Richards and co-workers⁴ but no clear conclusion could be reached except that in solution inequivalent CO and phosphine ligands appear to be present. Similarly we are unable to propose structures with any degree of certainty for the green complexes 6a and 6b isolated in the present work. The triethylphosphine complex 6a appears to have a non-linear trans arrangement of the two CO ligands about the metal centre since the IR spectrum shows one weak and one strong v(CO)mode near 1900 cm⁻¹, cf. 1, 4 and 5. Based on a distortedoctahedral geometry, two isomeric forms with a symmetric arrangement of the SC_6F_5 and PEt_3 are possible *cis*, **6(iv**), or trans, 6(v), each of which can have syn and anti forms. The ¹H and ¹⁹F NMR each show one set of ligand resonances indicating that only one of the two possible forms is present in solution. The ¹⁹F NMR spectrum however shows additional peaks on cooling to -50 °C, perhaps indicating the freezing out of syn and anti forms at low temperatures. However, these were not sufficiently well resolved for unambiguous conclusions to be reached.

The green isomer of complex **6b** was isolated pure from the reaction mixture with short reaction times but on dissolving in



 CD_2Cl_2 readily turns brown and eventually red. Infrared spectra taken in the solid state (Nujol) or immediately in solution (CCl₄) are similar to that of **6a**, but on placing under nitrogen two extra peaks at 1868s and 1938m cm⁻¹ similar to those for **6c** are observed suggesting isomerisation to give a mixture of green and red forms. It did not prove possible to obtain NMR spectra of a completely pure form, red or green so that conclusions concerning the structure are not possible. Further studies in this area of chemistry are currently in progress and hopefully these will help clarify this and other unresolved problems.

Experimental

The NMR spectra were recorded on a Bruker WP 200SY

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spectrometer at 200.13 (¹H), 188.3 (¹⁹F), 81.0 (³¹P) and 50.32 MHz (¹³C). Chemical shifts are referenced to SiMe₄ (¹H, δ 0) and CCl₃F (¹⁹F, δ 0). Infrared spectra were recorded as solutions on a Perkin Elmer 580 spectrophotometer with polystyrene as reference and mass spectra on a Vacuum Generators updated AEI MS 11 instrument. Reactions were carried out under dry, oxygen-free nitrogen using Schlenk techniques. Solvents were dried by refluxing over P₂O₅ (CH₂Cl₂), calcium hydride (hexane, diethyl ether) and distilled just before use. The complex [WBr₂(CO)₂(nbd)] was synthesised as described previously.³

Reactions of $[WBr_2(CO)_2(nbd)]$ 1.—With $Tl(C_5H_5)$. A mixture of complex 1 (37 mg) and $Tl(C_5H_5)$ (20 mg) in Et₂O (10 cm³) was stirred at room temperature for 18 h. The red-brown solution obtained after centrifuging was treated with hexane, concentrated *in vacuo* and cooled to -15 °C to give red crystals of $[WBr(CO)(nbd)(\eta^5-C_5H_5)]$ 2 (13 mg, 38%) (Found: C, 33.5; H, 2.75. C₁₃H₁₃BrOW requires C, 34.8; H, 2.9%; *m/z* = 449, M^+). IR(CHCl₃) 1928s cm⁻¹. ¹H NMR (CDCl₃): δ 5.44 (s, 5 H, C₅H₅), 3.60 (br m, 2 H, nbd), 3.49 (m, 2 H, nbd), 3.36 (m, 1 H, nbd), 2.65 (m, 1 H, nbd) and 1.11 (m, 2 H, nbd).

With Tl(O_2 CMe), 1:2 molar ratio. A mixture of complex 1 (29 mg) and Tl(O_2 CMe) (30 mg) in CH₂Cl₂ (3 cm³) was stirred at room temperature for 3 h. The yellow solution obtained on centrifuging the mixture was treated with hexane and concentrated *in vacuo* to give brown crystals of [WBr(O_2 CMe)(CO)₂-(nbd)] **3a** (6 mg, 22%) (Found: C, 27.3; H, 2.4. C₁₁H₁₁BrO₄W requires C, 28.1; H, 2.4%). IR (CCl₄): v(CO) 2056w and 1985s cm⁻¹.¹H NMR (CDCl₃, 20 °C): δ 3.81 (br s, 4 H, nbd), 3.30 (br s, 2 H, nbd), 1.87 (s, 3 H, O₂CMe) and 1.14 (pseudo q, 2 H, nbd).

With Tl[O(S)CMe], 1:3 molar ratio. A mixture of complex 1 (57 mg) and Tl[O(S)CMe] (100 mg) in Et₂O (3 cm³) was stirred at room temperature for 1 min. The yellow solution obtained on centrifuging was treated with hexane and concentrated *in vacuo* to give a yellow microcrystalline solid [WBr{O(S)CMe}(CO)₂-(nbd)] **3b** (25 mg, 44%) (Found: C, 27.5; H, 2.3. C₁₁H₁₁BrO₃SW requires C, 27.1; H, 2.3%; m/z = 459, $[M - CO]^+$). IR (CCl₄): v(CO) 2050w and 1982s cm⁻¹. ¹H NMR (CDCl₃): δ 3.85 (br s, 4 H, nbd), 3.24 (br s, 2 H, nbd), 2.09 [br s, 3 H, O(S)CMe] and 1.25 (pseudo q, 2 H, nbd).

With Tl(SC₆F₅), 1:1 molar ratio. A mixture of complex 1 (49 mg) and Tl(SC₆F₅) (42 mg) in CH₂Cl₂ (10 cm³) was stirred at room temperature for 10 min. A yellow-brown solution was obtained on centrifuging and on treatment with hexane and concentrating *in vacuo* brown crystals of [WBr(SC₆F₅)-(CO)₂(nbd)] **4** were obtained (48 mg, 79%) (Found: C, 29.7; H, 1.4; S, 5.1. C₁₅H₈BrF₅O₂SW requires C, 29.5; H, 1.3; S, 5.2%; m/z = 583, $[M - CO]^+$). IR (CCl₄): v(CO) 2055m and 1986s cm⁻¹. ¹H NMR (CDCl₃, -50 °C): δ 4.65 (br s, 1 H), 4.51 (br s, 1 H), 4.04 (br s, 1 H), 3.96 (br m, 1 H), 3.80 (br s, 1 H), 3.59 (br m, 1 H) and 0.98 (s, 2 H).

With an excess of Tl(SC₆F₅). A mixture of complex 1 (42 mg) and Tl(SC₆F₅) (81 mg) in CH₂Cl₂ (3 cm³) was stirred at room temperature for 18 h. The dark red solution obtained on centrifuging was treated with hexane, concentrated *in vacuo* and cooled to -15 °C to give red-brown crystals of [W(SC₆F₅)₂-(CO)₂(nbd)] **5** (40 mg, 67%) (Found: C, 34.3; H, 1.2. C₂₁H₈F₁₀O₂S₂W requires C, 34.5; H, 1.1%; *m/z* = 730, *M*⁺). IR(CCl₄): v(CO) 2040w and 1969s cm⁻¹. NMR (CDCl₃, 20 °C): δ 4.24 (t, J 2.5 Hz, 4 H), 3.84 (br s, 2 H) and 1.03 (s, 2 H); ¹⁹F, δ -134.1 (m, 4F), -155.73 (t, 2F) and -161.86 (m, 4F).

Reactions of $[W(SC_6F_5)_2(CO)_2(nbd)]$ 5.—*With* PEt₃. A solution of complex 5 (50 mg) in CH₂Cl₂ (10 cm³) was treated with PEt₃ (17 mg), when the colour changed from red to green. After 15 min hexane was added and the solution concentrated *in vacuo* to give green crystals of $[W(SC_6F_5)_2(CO)_2(PEt_3)_2]$ 6a (44 mg, 89%) (Found: C, 35.4; H, 3.6. $C_{26}H_{30}F_{10}O_2P_2S_2W$ requires C, 35.7; H, 3.5%). IR(CDCl₃): 1974vw and 1866s cm⁻¹. NMR(CD₂Cl₂, 20 °C): ¹H, δ 1.95, 1.83 (overlapping multiplets,

Table 2 Fractional coordinates for $[WBr(SC_6F_5)(CO)_2(nbd)]$ 4

Atom	x	у	z
W	-0.193 48(7)	0.230 35(6)	-0.24149(5)
Br	-0.01743(20)	0.361 28(18)	-0.20440(17)
S	-0.349 6(4)	0.240 7(4)	-0.1098(3)
F(2)	-0.3934(9)	0.019 8(8)	-0.073 0(8)
F(3)	-0.3180(11)	-0.0884(10)	0.096 6(9)
F(4)	-0.1881(11)	-0.0041(9)	0.262 3(9)
F(5)	-0.1299(13)	0.193 3(10)	0.256 8(9)
F(6)	-0.2000(12)	0.302 7(10)	0.087 3(9)
O(1)	-0.0055(12)	0.092 8(10)	-0.095 5(9)
O(2)	-0.3714(13)	0.386 3(11)	-0.3672(10)
C(1)	-0.3004(16)	0.166 2(14)	0.0014(12)
C(2)	-0.327 5(16)	0.064 6(14)	0.007 7(12)
C(3)	-0.289 5(17)	0.010 3(15)	0.094 2(14)
C(4)	-0.2243(16)	0.053 4(15)	0.177 6(13)
C(5)	-0.1941(18)	0.147 5(16)	0.172 8(15)
C(6)	-0.2323(17)	0.206 4(15)	0.086 6(13)
C(7)	-0.073 9(16)	0.139 4(14)	-0.149 8(13)
C(8)	-0.3044(17)	0.331 7(15)	-0.3166(13)
C(9)	-0.195 8(22)	0.057 1(18)	-0.4821(17)
C(10)	-0.128 7(19)	0.051 5(16)	-0.367 4(15)
C(11)	-0.2483(19)	0.076 8(16)	-0.2971(13)
C(12)	-0.324 3(18)	0.141 8(15)	-0.3592(14)
C(13)	-0.2526(19)	0.159 6(16)	-0.462 1(14)
C(14)	-0.1333(18)	0.217 1(15)	-0.4238(14)
C(15)	-0.054 9(16)	0.148 5(14)	-0.364 4(13)

12 H, CH₂) and 1.03 (apparent spt, 18 H, CH₃); 19 F, $\delta - 135.8$ (m, 4F), 159.23 (t, 2F) and 163.60 (m, 4F).

With PMe_2Ph . A solution of complex 5 (50 mg) in CH_2Cl_2 (10 cm^3) was treated with PMe₂Ph (20 mg) when the red colour slowly (10 min) turned green. Hexane (3 cm³) was added, the solution concentrated in vacuo and after cooling to -15 °C green crystals of $[W(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$ 6b were obtained (48 mg, 87%) (Found: C, 39.1; H, 2.4. $C_{30}H_{22}$ -F₁₀O₂P₂S₂w requires C, 39.4; H, 2.4%). IR(CCl₄): v(CO) 1877s cm⁻¹. NMR (CDCl₃, 20 °C): ¹H, δ 7.6–7.2 (m, 10 H, Ph) and 2.0 (overlapping signals, 12 H, Me); ${}^{19}F$, $\delta - 133.02$ (m, 4F), -159.33 (t, 2F) and -165.20 (m, 4F).

With P(OMe)₃. A solution of complex 5 (40 mg, 0.056 mmol) in CH₂Cl₂ (4 cm³) was treated with P(OMe)₃ (10 mg, 0.08 mmol) in a sealed tube and warmed to 60 °C for 1.5 h. The resulting red solution was filtered, treated with hexane (4 cm³), concentrated in vacuo and on cooling to -15 °C orange-red crystals of $[W(SC_6F_5)_2(CO)_2{P(OMe)_3}_2]$ 6c were obtained (36 mg, 74%) (Found: C, 26.5; H, 1.9. $C_{20}H_{18}F_{10}O_8P_2S_2W$ requires C, 27.1; H, 2.05%). IR(CCl₄): v(CO) 1978m and 1905s cm⁻¹. NMR: ¹H(CDCl₃, 20 °C), δ 3.70 (filled in doublet, Me); ¹⁹F (CD₂Cl₂, 20 °C), δ – 133.02 (m, 4F), –159.33 (t, 2F) and –165.20 (m, 4F); ¹³C-{¹H} (CDCl₃, 26 °C), δ 225.85 (t, J_{P-C} 73.5 Hz, CO), 150–135 (group of multiplets, C_6F_5) and 54.50 (s, Me); ${}^{31}P-{}^{1}H$ (CD₃Cl₂, -60 °C), δ 145.2 (s) and 144.7 (br s).

Structure Analysis.--Crystal data. C15H8BrF5O2SW, M = 611.04, monoclinic, space group $P2_1/n$, a = 10.040(4), \dot{A}^{3} , Z = 4, $D_{c} = 2.404$ g cm⁻³, F(000) = 1136, Mo-K α X-rays, $\lambda = 0.710$ 69 Å, $\mu = 95.1$ cm⁻¹.

Measurements were made with a plate-shaped crystal of dimensions $0.36 \times 0.16 \times 0.02$ mm mounted on an Enraf-Nonius CAD4 diffractometer. The intensities of 3794 reflections with $2 \le \theta \le 24^\circ$, h 0–11, k –15 to 4 and l –14 to 14 were estimated from ω -2 θ scans. Lorentz polarisation and empirical absorption corrections²⁸ (correction factors 0.80-1.30) were applied and equivalent reflections then merged ($R_{int} = 0.063$ for 1050 duplicate measurements) to give 2640 unique structure amplitudes of which 1587, with $I \ge 3\sigma(I)$, were used subsequently.

The structure was solved by Patterson and Fourier methods.

The final full-matrix least-squares refinement on F of 116 parameters, including anisotropic displacement parameters only for W, Br and S atoms, converged at R = 0.052 and R' =0.057 with $w = 1/\sigma^2(F)$, see Table 2. Hydrogen atoms were placed in stereochemically acceptable positions and constrained to ride on their parent C atoms with C-H 0.96 Å and $U(H) \approx 1.2U(C)$. Final $\Delta \rho$ values were between 2.3 and -1.6 e Å⁻³. All calculations were performed with the GX package²⁹ using scattering factors and anomalous dispersion corrections from ref. 30.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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